PB84-226489

Organic Pollutant Sorption in Aquatic Systems

(U.S.) Environmental Research Lab., Athens, GA

1984

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. PB84-226489
EPA-600/J-84-052		

4. TITLE AND SUBTITLE	5. REPORT DATE
Organic Pollutant Sorption in Aquatic Systems (Journal Version)	1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Samuel W. Karickhoff	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Environmental Research Laboratory U.S. Environmental Protection Agency College Station Road Athens GA 30613	AARB1A
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
U.S. Environmental Protection Agency--Athens GA Office of Research and Development Environmental Research Laboratory Athens GA 30613	Journal article
	14. SPONSORING AGENCY CODE
	EPA/600/01

15. SUPPLEMENTARY NOTES
Published in Journal of Hydraulic Engineering. 110(6):707-735, 1984
Contact: S.W. Karickhoff 8-250-3149

16. ABSTRACT

An understanding of sorption processes is an important key to describing pollutant fate in an aquatic system because sorption may alter significantly physical transport and chemical reactivity of pollutants. The sorption of uncharged organic to natural aquatic sorbents is dominated by "hydrophobic interactions." For composite particulates (i.e., sediments/soils), organic matter is the primary sorbing constituent. Sorption partition coefficients, indexed to organic carbon (K_{oc}), are relatively invariant for natural sorbents. K_{oc}'s can be estimated from other physical properties of pollutants (aqueous solubility or octanol/water partition coefficients). Hydrophilic contributions to sorption tend to occur with one or both of the following conditions: (1)high sorbate polarity; and (2) low organic carbon content of the sorbent, especially with coincident high clay content. Although a priori estimation techniques comparable to hydrophobic sorption are not presently available, hydrophilic contributions relative to K_{oc} can be estimated based on chemical class and sorbent composition. Although sorption to sediment or soils is frequently viewed as a rapid process in environmental modeling, true sorption equilibrium may require weeks to months to achieve with pollutant uptake and release kinetics highly dependent on molecular size, sorbent cohesive properties, and solids concentration.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	31
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (9-73)

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

EPA-600/J-84-052
JOURNAL ARTICLE

ORGANIC POLLUTANT SORPTION IN AQUATIC SYSTEMS

By Samuel W. Karickhoff[1]

ABSTRACT: An understanding of sorption processes is an important key to describing pollutant fate in an aquatic system because sorption may alter significantly physical transport and chemical reactivity of pollutants. The sorption of uncharged organic chemicals to natural aquatic sorbents is dominated by "hydrophobic interactions." For composite particulates (i.e., sediments/soils), organic matter is the primary sorbing constituent. Sorption partition coefficients, indexed to organic carbon (K_{oc}), are relatively invariant for natural sorbents. K_{oc}'s can be estimated from other physical properties of pollutants (aqueous solubility or octanol/water partition coefficients). Hydrophilic contributions to sorption tend to occur with one or both of the following conditions: (1) High sorbate polarity; and (2) low organic carbon content of the sorbent, especially with coincident high clay content. Although a priori estimation techniques comparable to hydrophobic sorption are not presently available, hydrophilic contributions relative to K_{oc} can be estimated based upon chemical class and sorbent composition. Although sorption to sediment or soils is frequently viewed as a rapid process in environmental modeling, true sorption equilibrium may require weeks to months to achieve, with pollutant uptake and release kinetics highly dependent on molecular size, sorbent cohesive properties, and solids concentration.

FORWARD

This paper was solicited by the ASCE Hydraulics Division Committee on Hydrologic Transport and Dispersion. It is the first of several state-of-the-art papers addressing aquatic transport and mixing problems faced by civil engineers. The present topic was selected for two reasons: (1) The importance of sorption processes in determining the fate of organic pollutants, and (2) the desire to integrate a rapidly expanding collection of data in a forum available to hydraulic modelers.

INTRODUCTION

Pollutant fate in natural waters is highly dependent on sorptive behavior. In addition to an obvious effect on physical transport, sorption can be involved directly or indirectly in pollutant degradation. The chemical reactivity of a pollutant in a sorbed state may differ significantly from that in aqueous solution, both in extent and chemical pathway (36,46,64). Moreover, natural sorbents may indirectly mediate solution phase processes by altering the solution phase pollutant concentration or by controlling pollutant release into the aqueous phase and thereby potentially rate-limiting solution phase reaction. In addition, natural sorbents "introduce" into solution a "buffered" suite of inorganic and organic species that can significantly affect pollutant reac-

[1]Research Chemist, U.S. EPA, Environ. Research Lab., College Station Road, Athens, Ga. 30613.

Note.—Discussion open until November 1, 1984. To extend the closing date one month, a written request must be filed with the ASCE Manager of Technical and Professional Publications. The manuscript for this paper was submitted for review and possible publication on January 3, 1983. This paper is part of the *Journal of Hydraulic Engineering*, Vol. 110, No. 6, June, 1984. ©ASCE, ISSN 0733-9429/84/0006-0707/$01.00. Paper No. 18939.

of Hydraulic Engineering, 110(6):707-735, June 1984

tivity in the aqueous phase. An important key to describing pollutant fate in aquatic systems is an understanding of these sorptive processes.

Natural sorbents may be biotic and abiotic; may be organic, inorganic, or chemical composites thereof and may range in size from macromolecules to gravel. Organic pollutants vary in size (single carbon to macromolecular compounds) and in water solubility from complete miscibility to virtual insolubility. This high degree of variability and complexity in sorbent/sorbate composition, chemical character, and potential sorptive interactions seems to preclude the development of simplistic sorption models for aquatic systems with any degree of theoretical legitimacy. The key to such model development involves discriminating initially the essential phenomenological behavior (trends) while neglecting what could be termed "second-order" effects or incidental details. These "idealized" models can then be made more general by the addition of "corrective terms" that hopefully can be causally related to those details neglected in the idealization process.

A fundamental prerequisite to model development is definition of purpose. Model structure (i.e., mathematical format and degree of abstraction, level of temporal and spatial detail, and requirement for supporting physical rationale) is intimately a function of intended use. The surface water sorption models described herein are designed for what might be loosely characterized as engineering applications, and can serve the following purposes: (1) A priori estimation of pollutant sorption behavior using commonly measured (or computed) physical properties of pollutant and sorbent, and incorporating commonly measured environmental variables; (2) guidance for ordering, interpreting, and in a non-rigorous sense "understanding" existing data; (3) evaluation or screening of existing data based on "expected" behavior; and (4) extrapolation of sorption measurements (field or laboratory) outside the domain of measurement.

For the most part, model validity derives more from long-term accretion of phenomenological evidence than from mechanistic rigor. Physical rationale is offered, however, in support of mathematical functionality, and is used to define (or extend) appropriate models in instances where the current state of knowledge or available data are insufficient for model definition. It should be stated at the outset that the prescribed usage precludes the utilization of regression equations developed and calibrated for site-specific circumstances.

Manuscript Scope.—Natural sorbents addressed include sediments, microorganisms, and "dissolved" humic material. With the exception of aquatic plants and higher order animals, these natural materials encompass essentially all potential aquatic sorbents. Natural sediments are inorganic minerals (the surfaces of which largely are coated with inorganic and organic polyelectrolytes or slimes) and organic detritus. Organic chemicals reviewed include organic cations and neutral organic compounds of limited water solubility ($<10^{-3}\,M$). These two categories cover essentially all organic pollutants for which sorption might be expected to contribute to environmental fate/impact in aquatic systems.

This framework for reviewing sorption in natural aquatic systems excludes waste-dump applications typically involving complex chemical mixtures and high pollutant concentrations. Pollutant concentrations in

the aqueous phase are assumed to be typical of ambient environmental levels (low parts-per-million and/or well below aqueous solubility limits). It is assumed that in cases involving point pollutant discharges or pesticide runoff (where pollutant input concentrations may be high), dilution in the receiving waters will rapidly reduce the pollutant levels below the specified maxima.

Although the primary emphasis in this paper is on sorption equilibrium, sorption to natural sediments frequently involves a "nonlabile" component. Physical rationale is offered for this process and appropriate kinetic models are discussed.

Equilibrium Sorption—Partition Coefficient

Equilibrium sorption is described graphically by a sorption isotherm, which is a plot of pollutant concentration in the sorbed phase (denoted S) versus pollutant concentration in solution (C). Sorption isotherms are typically measured at constant temperature and at constant sorbent concentration.

Thermodynamically, sorption equilibrium can be defined as the state at which the pollutant fugacities in the sorbed and solution phases are equal

$$f^s = f^w \quad (1)$$

in which the superscripts s and w refer to the sorbed and solution phases, respectively. [Mackay (37) has described the use of fugacity in environmental systems.]

Moreover, even if the sorbent, such as a sediment, is pictured as a composite mixture of different sorbents, the fugacity within each sorptive compartment must be equal at equilibrium. $f_i^s = f^w$ for all sorptive compartments (i). The fugacity or "escaping tendency" can be related to pollutant concentration in each phase. For example, for the aqueous phase

$$f^w = \phi^w C \quad (2)$$

The fugacity coefficient (ϕ^w, ϕ^s) is commonly expressed as the product of an activity coefficient (γ) and the corresponding reference state fugacity (f_o). This fugacity coefficient is the reciprocal of the fugacity capacity (Z) used by Mackay (37). That is

$$\phi^w = \gamma^w f_o^w = Z_w^{-1} \quad (3)$$

The numerical evaluation of any given coefficient (ϕ) requires the specification of the standard or reference state and its associated fugacity. Aqueous phase pollutant concentrations are conventionally expressed relative to aqueous phase volume, and sorbed concentrations are referenced to dry mass sediment/soil.

For the sorbent "mixture," the sorbed pollutant concentration can be taken as a weight-averaged sum of the components.

$$S = \sum_i Y_i S_i = f^s \sum_i \frac{Y_i}{\phi_i^s} \quad (4)$$

in which Y_i denote component weight fractions. The sorbed and solution

pollutant concentrations are related by

$$S = C\frac{\phi^w}{\phi^s} \quad (5)$$

In general, fugacity coefficients are dependent on pollutant concentration and, therefore, the corresponding sorption isotherms are nonlinear. In sufficiently dilute systems, however, these coefficients approach limiting values and the isotherms approach linearity. In simplistic terms, this is the limit in which solute-solute interactions can be ignored in each phase; the molecular environment of the pollutant within each phase remains relatively constant with changes in solute concentration.

It is this "lowloading" limit that should be quite typical of most environmental situations

$$S = K_p C \quad (6)$$

$$\text{in which} \quad K_p = \frac{\phi^w}{\phi^s} \quad \text{or} \quad K_p = \phi^w \sum_i \frac{Y_i}{\phi_i^s} \quad \text{(for composite sorbents)} \quad (7)$$

K_p = the sorption partition coefficient, and the fugacity coefficients are low-concentration limiting values. By convention, concentration units are chosen with the volume unit in solution equivalent in mass to the mass unit for sediment; typical units for K_p are therefore L/kg or ml/g.

How dilute the system must be to show this limiting behavior varies from system to system, depending on the nature of the solute and sorbent and on the type of sorption interaction. Just as in gas-liquid equilibria, where rough rules for adherence to Henry's law can be formulated in terms of solute solubilities and partial pressures (47), it has been determined (29) for hydrophobic compounds that, if the equilibrium aqueous phase pollutant concentration is below 10^{-5} M or less than one half of the solute water solubility (whichever is lower), sorption isotherms to natural sediments are linear. More recent works, (9,13,22, 23,38,39,50) substantiate this low-loading isotherm linearity for hydrophobic compounds. For nonhydrophobic bonding, low-loading isotherm linearity is frequently observed also (41). Unfortunately, conditions for linearity may involve sorbent and solution phase chemistry in addition to pollutant loading and, therefore, cannot be specified as simply as in the "hydrophobics" case. (This is reviewed in subsequent sections.) A potentially important source of observed isotherm nonlinearity is solute speciation changes (aggregation, proton gain or loss, chemical complexation or degradation) not explicitly accounted for or experimentally measured or controlled.

It should be emphasized that "sorbed state" concentrations, and thermodynamic variables derived therefrom, are operationally defined. Sorbed concentrations are commonly referenced to total sorbent mass (as specified for S) or to the mass of a specific component of the sorbent (i.e., S_i). Seldom can the actual distribution volume of the sorbate be defined, however; nor is the uniformity or anisotropy of the sorbate distribution typically known. Thermodynamic properties derived from these measurements are highly dependent in numerical value on computational prescription, and care must be exercised in mechanistic implications derived therefrom. Exceptions are thermodynamic properties pertaining to

the sorbed state but fixed in value, relative to the aqueous phase, by equilibrium constraints (i.e., chemical potential, fugacity, temperature, etc.).

Sediment Sorption of Uncharged Organic Chemicals—Dependence on Organic Carbon

From pesticide-soil studies, numerous soil properties [organic carbon content, particle size distribution, clay mineral composition (amount and type), pH, cation-exchange capacity (CEC)] have been identified as affecting the type (mechanism) and degree of pesticide sorption (1,2,8, 10,18,20,21,28,41,55,57,58). The predominance of organic carbon in "controlling" the sorption of uncharged organic compounds, however, has been extensively documented for soils (2,13,30,48,50,57,58,59) and more recently confirmed for sediments (9,23,27,29,51,52). This suggests that the partition coefficient for a sediment consisting of multiple sorbent components (i.e., Eq. 7) can be reduced (in a first approximation) to a form containing only sorption to organic matter.

$$K_p \simeq \phi^w \frac{oc}{\phi^{oc}} \quad \ldots\ldots (8)$$

in which organic matter is expressed as fraction organic carbon, oc. The fugacity coefficient ratio is typically defined as K_{oc}.

$$K_{oc} \cong \frac{\phi^w}{\phi^{oc}} \quad \ldots\ldots (9)$$

"Carbon-referenced sorption" has been tested for a wide variety of both compounds and sediment/soils. Most notable documentation is contained in Walker and Crawford [59 (triazines, 32 soils)], Talbert and Fletchall [55 (triazines, 25 soils)], Karickhoff [27 (polynuclear aromatics, 17 sediments/soils)], and Hassett et al. [23 (polynuclear aromatic and related heterocyclic organics, 14 sediments/soils)]. From these findings, combined with the data compilations on pesticide/soil sorption by Rao et al. (48) and Framer (16), it can be safely generalized that for uncharged organic compounds of limited water solubility ($<10^{-3}$ M) that are not susceptible to speciation changes or other special complex formation in the sediment suspension of interest, sorption is typically "controlled" by organic carbon and is amenable to the K_{oc} format of quantification.

Estimation of K_{oc}.—As described in the previous section, K_p estimation for uncharged "organics" can typically be reduced to estimation of K_{oc}, which, when combined with organic carbon content of the sediment, can yield a good estimate of the sediment-water partition coefficient (K_p) (Eqs. 8 and 9). The K_{oc} can be expressed as the ratio of solute fugacity coefficients in the aqueous, ϕ^w, and organic matter, ϕ^{oc} phases (Eq. 9) or in terms of activity coefficients.

$$K_{oc} \propto \frac{\gamma^w}{\gamma^{oc}} \quad \ldots\ldots (10)$$

in which the proportionality constant contains the reference state fugacity and unit conversion factors for pollutant concentrations. For hy-

drophobic materials, a convenient reference state is the pure liquid (or subcooled liquid) at STP. Because the activity coefficient "contrasts" adhesive (solvent-solute) and cohesive (solute-solute) interactions in a given phase with the cohesive interactions in the solute reference state (i.e., pure liquid), one would expect highly nonideal behavior in the aqueous phase with large variations in γ^w from solute to solute (comparable to differences in aqueous phase solubility). To the contrary, in the sorbed state the adhesive (i.e., sorptive) interactions with the organic matrix could be assumed to be quite similar in type and magnitude to cohesive interactions in the pollutant reference state. Variations in γ^∞ from solute to solute would be largely entropic in nature and would be comparable to changes in solute molar volume [as prescribed by the Flory-Huggins relationship (17)]. In going from benzene to benzpyrene, for example, one would expect approximately a fourfold increase in γ^∞, compared to an increase in γ^w of roughly four orders of magnitude. Thus for a series of hydrophobic organics, variations in K_∞ would be dominated by variations in the aqueous phase activity coefficient.

$$K_\infty \propto \gamma^w \quad \ldots\ldots (11)$$

K_∞ from Water Solubility.—For hydrophobic liquids, γ^w is equal to the reciprocal of the mole fraction solubility, X_s. For solids, a crystal energy term must be added, which gives in an approximated form [see Prausnitz (47) for a more complete expression]:

$$\log \gamma^w = -\log X_s - \frac{\Delta S_f (T_m - T)}{2.303\, RT} \quad \ldots\ldots (12)$$

in which ΔS_f = the solute entropy of fusion, T_m = the melting point in °K, T = absolute temperature, and R = the gas constant. For liquids (i.e., $T > T_m$), T is set equal to T_m and the crystal term vanishes. Yalkowsky and Valvani (63,64) have reviewed, in detail, estimation of ΔS_f. For "rigid" organic molecules which are solids at 25° C, ΔS_f is not highly variable 12–15 eu (entropy units, cal/mole K°). Rigid molecules include cyclic compounds (aliphatic or aromatic) and molecules containing less than five atoms in a flexible chain. Fortunately, nonrigid molecules typically melt at much lower temperatures than rigid molecules of similar molecular weight and are frequently liquids at room temperature; for most pollutants of this type, the "crystal term" is either zero or very small.

Expressing ϕ^∞ in terms of readily accessible molecular properties is not so straightforward. With regard to K_∞ estimation, however, variation in ϕ^∞ from solute to solute is presumed to be of secondary importance and can be implicitly factored into the solubility dependence by empirically fitting observed sorption data to an equation of the form

$$\log K_\infty = -\alpha \log X_s - \frac{\Delta S_f (T_m - T)}{2.303\, RT} + \beta \quad \ldots\ldots (13)$$

in which α and β are regression-fitted parameters. The deviation of α from unity reflects variation in ϕ^∞ for the basis set of compounds.

An equation of this form has been applied to condensed ring aromatics (27) giving:

$$\log K_\infty = -0.921 \log X_s - 0.00953\,(\text{mp} - 25) - 1.405 \quad \ldots\ldots (14)$$

in which ΔS_f is taken to be 13.0 eu; mp is the melting point in °C. This equation was examined using literature data for other families of hydrophobic organics (triazines, carbamates, organophosphates, chlorinated hydrocarbons), and was found to estimate K_{oc} generally within a factor of 2–3 of measured values. For chlorinated hydrocarbons, however, the equation worked well for low molecular weight compounds (both aliphatic and aromatic) but tended to overestimate (by as much as an order of magnitude) sorption of highly chlorinated, high molecular weight compounds (such as DDT or hexachlorobiphenyls). This suggests that the α coefficient (Eq. 13) for this class of compounds may be considerably less than the polynuclear-aromatic-hydrocarbon (PNA) value, apparently in the range of 0.7–0.8. It is uncertain whether this deviation derives from kinetic or steric inhibition of sorption or decreased affinity for natural organic matter (i.e., increase in ϕ^{oc}). If the literature data [catalogued in Karickhoff, (27)] for five chemical families are fitted to Eq. 12, the resulting equation is

$$\log K_{oc} = -0.83 \log X_s - 0.01(\text{mp} - 25) - 0.93$$

$$(47 \text{ compounds}, r^2 = 0.93) \quad \ldots\ldots (15)$$

K_{oc} from K_{ow}.—The octanol/water partition coefficient (K_{ow}) like K_{oc} is a distribution coefficient of solute monomers between an aqueous phase and a hydrophobic organic phase. Thermodynamically K_{ow} can be expressed as the ratio of activity coefficients if the same standard state is chosen in each phase (i.e., pure subcooled liquid solute)

$$K_{ow} = \frac{C_o}{C_w} = \frac{\phi^w}{\phi^o} = \beta \frac{\gamma^w}{\gamma^o} \quad \ldots\ldots (16)$$

in which o and w = the octanol and aqueous phases, respectively; β is a unit adjustment constant converting C_o and C_w to mole fraction units in each phase. As was the case in sediment/water systems, γ^w can be considered to be the distilled water activity coefficient, unaffected by the presence of octanol (approximately 10^{-3} M at 25° C) in the aqueous phase.

By combining Eqs. 9 and 16, K_{oc} and K_{ow} are related by

$$K_{oc} = \frac{\phi^o}{\phi^{oc}} K_{ow} \quad \ldots\ldots (17)$$

in which the proportionality constant is the ratio of fugacity coefficients for the solute dissolved in octanol (*saturated with water*) and bound in natural organic matter. For K_{oc} and K_{ow} to be linearly related, this ratio must be independent of solute.

In numerous studies involving a wide variety of chemicals, the correlation between K_{oc} and K_{ow} has been examined (6,7,9,23,27,29,30, 48,51,52). Typically a linear regression equation of the following form is used:

$$\log K_{oc} = \alpha \log K_{ow} + \beta \quad \ldots\ldots (18)$$

in which α and β are data-fitted coefficients. The result is a somewhat divergent group of relationships. Several factors contribute to this variability:

1. Hydrophilic contributions to sorption, the thermodynamic rationale for relating K_{oc} to K_{ow} is predicated on: (1) The predominance of organic carbon as the key sorbent component of soils and sediments; (2) the predominance of hydrophobic sorption (as opposed to polar group interactions, ionic bonding, or chemisorption); and (3) sorption linearity. The impact of hydrophilic factors on the observed K_{oc} is more in evidence for molecules containing polar functional groups, which tend to be those with lower K_{ow}'s (10^3 or less).

2. Kinetic or steric inhibition of sorption, for many sorbate/sediment systems, true sorption equilibrium may require weeks or longer. The phenomenon appears to be one of solute access to sorbent and is especially in evidence for large molecules. The net effect is an apparent reduction in K_{oc} when sorption is measured over short time frames (hours).

3. Use of computed K_{ow}'s, substituent or fragment constants determined for small or monosubstituted molecules frequently do not work well for either large molecules or molecules with multiple substituents, resulting frequently in overestimates of K_{ow}.

The combined effect of these three factors is illustrated in Fig. 1 where deviations from hydrophobic sorption are indicated by hatched areas. These factors are reviewed in detail in subsequent sections.

Published equations "calibrated" on sets of *hydrophobic* compounds include the following:

Ref. 52: $\log K_{oc} = 0.72 \log K_{ow} + 0.49$ (predominately methylated and halogenated benzenes, 13 compounds, $r^2 = 0.95$) ..... (19)

Ref. 48: $\log K_{oc} = 1.029 \log K_{ow} - 0.18$ (13 pesticides, $r^2 = 0.91$) (20)

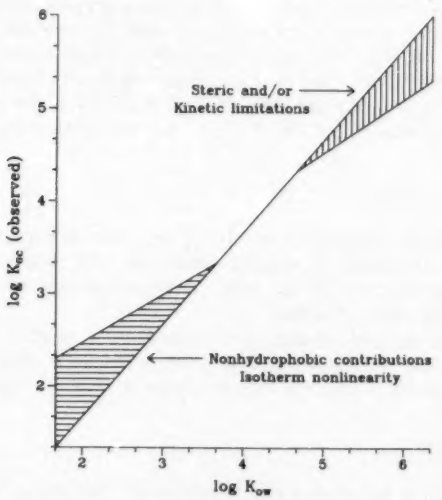

FIG. 1.—K_{oc}: Extrapolation from K_{ow}

Ref. 27: $\log K_{oc} = 0.989 \log K_{ow} - 0.346$ (5 pna's, $r^2 = 0.997$) ..... (21)

Ref. 23: $\log K_{oc} = \log K_{ow} - 0.317$ (pna's and substituted pna's, 22 compounds, $r^2 = 0.98$)..... (22)

A Priori K_{oc} Estimation from Molecular Fragments.—For computing thermodynamic properties, it has often been found useful to consider a molecule as a collection of molecular fragments, each making a distinct contribution to the thermodynamic property, which is relatively independent of the rest of the molecule. The most common application of this general concept is Linear Free Energy Theory (LFET), which frequently has been applied to solute partitioning between phases [i.e., chromatography (3), octanol/water partitioning (34,35), and even sorption to soils (33)]. The rationale behind the method is that a large number of molecular structures can be generated from a relatively small number of fragments, and thus a larger number of thermodynamic estimates can result from a small number of experimental measurements (fragment constants). The accuracy of the prediction, however, necessarily improves as the specificity of the fragment environment increases, which entails an increase in the number of fragments (or corrective factors) that must be considered. Practicality necessitates a compromise. In any given application, this theory is applied at different levels of sophistication. One user may employ a few fragment constants and generate "first-order" estimates whereas another may employ numerous corrections or adjustments reflecting more fragment specificity for a given molecular environment. For multiply substituted compounds, good estimates generally require sophisticated input, either in terms of system specific fragment constants or corrective terms. This approach, however, can permit facile extrapolation of K_{oc} measurements in some instances.

1. Addition of ring fragments. For unsubstituted condensed ring aromatics, the equation can be written as:

$$f^{\alpha}_{C_4H_2} = \log K_{oc}(\text{naphthalene}) - \log K_{oc}(\text{benzene}) \approx 1.16 \text{ (Ref. 27)} \ldots . \quad (23)$$

in which $f^{\alpha}_{C_4H_2}$ = the ring fragment constant for α condensed ring addition (i.e., fragment attached at α carbons). With this fragment constant, one can extrapolate to other condensed ring systems. For 3-ring systems, phenanthrene and anthracene, the computed value is 4.10 compared to the measured log K_{oc}'s of 4.03 and 4.20 (27), respectively. For 4 and 5-ring systems, the computed values are 5.26 and 6.42; measured values are 5.81 (29) for tetracene (4 ring) and 6.22 (23) for dibenz[*a*,*h*] anthracene (5 ring). Similarly, fragment constants can be derived for ring addition involving three carbon addition (β condensation) and two carbon addition (γ condensation), which would enable K_{oc} estimation for most condensed (6 membered ring) aromatic hydrocarbons.

2. Addition of functional groups. The addition of a functional group [(*X*) (replacing a H atom)] to a hydrocarbon matrix (*R*-H) is a primary application of LFET. In this case

$$\log K_{oc}(R\text{-}X) - \log K_{oc}(R\text{-H}) = \pi^{s}_{x} \ldots . \quad (24)$$

The substituent constants, π^{s}_{x}, are determined experimentally and are

relatively system independent for similar organic molecules. System specificity can be especially large for: (1) Addition of polar functional groups $-NH_2$ and $-OH$; (2) addition of electron releasing or withdrawing groups to compounds that can potentially ionize in sediment/water systems; and (3) multiple substitution of functional groups on a hydrocarbon matrix. Although this approach is not easily adaptable to a priori estimation of K_{oc} for most pesticides, it does offer considerable potential for mono- and di-substituted compounds. In this respect, tremendous advantage can be derived from the relationship between K_{oc} and K_{ow} described in the previous section (Eqs. 17–22). Because K_{oc} and K_{ow} are approximately linearly related, it can easily be shown that the substituent constants, π_x^s, for sorption approximate those for the comparable K_{ow} system, π_x^o. This makes possible the use of this extrapolation procedure without development of an extensive library of substituent constants, π_x^s. The comparable K_{ow} constants, π_x^o, are readily available (34,35) and are generally applicable excepting those instances described previously. It should be emphasized that this extrapolation does not require a knowledge of K_{ow} for either of the specific compounds R-H or R-X in question.

Gel Permeation Model for Hydrophobic Sorption

Recently, Freeman and Cheung (17) have applied solubility parameter theory to organic carbon—controlled sorption to natural sediments. Natural organic matter in sediment was pictured as a humic-kerogen gel affixed to mineral surfaces, and sorptive processes (kinetic and equilibrium) were described in terms of the diphasic liquid-gel-solute interactions.

$$\ln K_{oc} = A - BL_i + \frac{V_i}{RT} f(\delta) \quad \ldots\ldots (25)$$

in which the sediment parameters A and B depend upon pore structure within the sorbent gel, L_i is the size of the solute, V_i is the solute molar volume, and $f(\delta)$ is the solubility parameter function that expresses the solute preference for the liquid versus gel phases as given by

$$f(\delta) = (\delta_i - \delta_m)^2 - (\delta_i - \delta_g)^2 \quad \ldots\ldots (26)$$

in which the subscripts i, m, g = the solute, solvent and gel phases, respectively. This approach has been applied to only one sediment, and thus the sediment variability of A, B, and δ_g has not been determined. Also, there is a paucity of solubility parameter data for pollutants. A most notable advantage of this approach is the facile extension to nonaqueous or mixed solvents, requiring only the adjustment of the solvent solubility parameter, δ_m.

Sorption to Microorganisms and Dissolved Humics

For hydrophobic "organics," sorption to microorganisms and colloidal humic material is amenable to this same thermodynamic treatment and should lead to similar estimation equations. Relationships have been developed for mixed microbial populations, relating sorption to both water

solubility and octanol/water partition coefficients (4,53). It is noteworthy that if sorption is referenced to carbon (as opposed to bacterial mass), partition-coefficients to bacteria approximate sediment derived K_{oc}'s.

In the case of "prepared" humics (i.e., isolated from soil/sediment aggregates), "sorption" appears sensitive to both the source and mode of preparation (11,24,31,45,54). Insufficient data exist to formulate estimation equations but octanol/water partition coefficients can be taken as numerical upper limits for association of hydrophobic pollutants to natural humics.

Nonhydrophobic Bonding

For the vast majority of uncharged pollutants "carbon referenced" sorption is appropriate and the estimation techniques detailed previously for hydrophobic sorption give good estimates of "low loading" linear partition coefficients for natural sediments. Nonhydrophobic interactions, however, may contribute to (or dominate) sorption in some instances, a point that was stressed in a recent review by Mingelgrin and Gerstl (41). This tends to occur in coincidence with one or both of the following conditions: (1) High sorbate polarity, highly polar or ionizable functional groups conducive to significant site-specific bonding with polar groups or charged sites on sorbent surfaces; and (2) low organic carbon content in the sorbent, especially with coincident high clay content.

Unfortunately, the state-of-science does not permit a priori sorption estimation comparable to hydrophobic bonding in this instance. A prescriptive format is offered, however, for a logical mathematical approach, and specific examples are discussed where quantification is possible.

Multiple-Sorptive Processes.—A "complicative" feature in common occurrence with nonhydrophobic sorption is multiple sorptive contributions. This may involve binding to different sorbent components (mineral versus organic carbon), or may involve multiple binding mechanisms to a single component. It often is convenient to factor individual processes and treat each separately, but care must be exercised in combining the processes to obtain the integrated behavior. The key criterion determining the proper combinatorial algebra for multiple binding contributions is the presumed *distribution volume* of the pollutant in the sorbed state. That is, over what actual volume of the sorbent is a pollutant (sorbed by a particular mechanism) distributed. For example, carbon-referenced sorption (K_{oc}) assumes the sorbate distribution volume to be the organic matter fraction—likewise, sorption to minerals would involve all or some portion of the mineral fraction. Sorption contributions derived from processes occurring in different distribution volumes can be assumed to be independent and thus should be combined linearly (i.e., Eq. 7).

$$K_p \text{ (observed)} = \sum_j Y_j K_j \quad \ldots\ldots\ldots\

mechanisms acting in concert within the same distribution volume, however, a conventional method of factoring would presume the sorption energies to be additive and, therefore, the factored contributions to the equilibrium constant would be log-additive.

As mentioned previously, no definitive work has been done in either: (1) Determining the actual distribution volumes for sorbed pollutants; or (2) factoring multiple sorptive processes *quantitatively*.

Unfortunately, very few sorption data have been collected in such a manner to facilitate examination of such factoring. Initially, one could assume that sediment consists of only two sorbing components, inorganic mineral surfaces and organic matter (although one may choose to further subdivide or refine the definition of each).

Role of Minerals in Pollutant Sorption.—Perhaps the most extensively researched aspect of pollutant sorption involves pesticide-clay mineral interactions. Although highly elegant in many respects, this work is largely irrelevant to the present application. In the vast majority of such studies, the mineral surfaces were "cleaned" (highly prepared), whereas mineral surfaces, aged in aquatic systems, are covered with a wide variety of coatings, including organic slimes, microbial biomass, humic substances, and polymeric oxides and hydroxides. Unfortunatly, for one who seeks to extrapolate to a natural sediment, these coatings, which can be loosely classified as organic or inorganic polyelectrolytes, mask in a large part the true mineral sorption properties.

In studies where soils or sediments were used, a common procedure for factoring individual sorption contributions involves sequential removal of various components and subsequent sorption measurements. Although providing considerable insight into relative sorption affinities, these fractionation procedures may change the physical/chemical character of the isolated component(s) and undoubtedly will alter the "availability" of a particular component(s) relative to the parent material.

Sorbent "availability" is an important point in question. A commonly held viewpoint has the mineral fraction of most soils or sediments *unavailable* for pollutant sorption due to "blockage" by organic carbon (18,59). Similarly, one could also postulate an analogous reduction in organic carbon "availability" when incorporated into soil or sediment aggregates.

In order to factor and quantify component contributions to sorption, not only must the sorption properties inherent to given components be quantified, but the role of composite particles or aggregates in mediating sorbent "activity" must be defined. That is

$$K_p = K_m cm f_a^m + K_{oc} oc f_a^{oc} \quad \ldots\ldots\ldots\

variability (less than a factor of 2) on the same sediments/soils (23,27). This suggests kinetic or steric inhibition of sorption (i.e., a dependence of sorbent availability on sorbate size). Other recent findings (14,19, 44,56,61) indicate rather dramatic increases in sorption at very low sediment concentrations (<100 ppm dry weight solids), which may derive from break-up of sediment aggregates—increasing the availability of *both* mineral and organic sorbents.]

In the context of this paper, mineral sorption derives from an organic-free, *aged* mineral surface, a large portion of which may be coated with amorphous oxides and hydroxides. Eq. 28 describes mineral sorption by a single term, whereas sediments normally contain numerous minerals. With respect to sorption of organic chemicals, however, surface area is the primary property distinguishing various minerals, with "swelling clays" (i.e., montmorillonite, hectorite, etc.) dominating sorption in mixed mineral suites (23,28). Therefore, as a first approximation, mineral sorption can be indexed to swelling clay content. Hassett, et al. (23) observed, for a broad range of sediments and organic sorbates, that failure of organic carbon referenced sorption (i.e., the existence of a significant mineral contribution) was related to the relative amounts of swelling clay and organic carbon (cm/oc) present. This functional dependence can be shown by rearranging Eq. 28 to give $K_{p/oc} = K_{oc} + K_m f_a^{cm}\, cm/oc$ in which mineral contributions are evidenced by deviation in $K_{p/oc}$ relative to K_{oc}. Fig. 2 contrasts biquinoline and pyrene; observed partition coefficients expressed relative to organic carbon ($K_{p/oc}$) are plotted as a function of the relative amounts of swelling clay and organic carbon in the sediments. Biquinoline shows a substantial mineral contribution with increasing relative mineral content, whereas pyrene shows only a slight

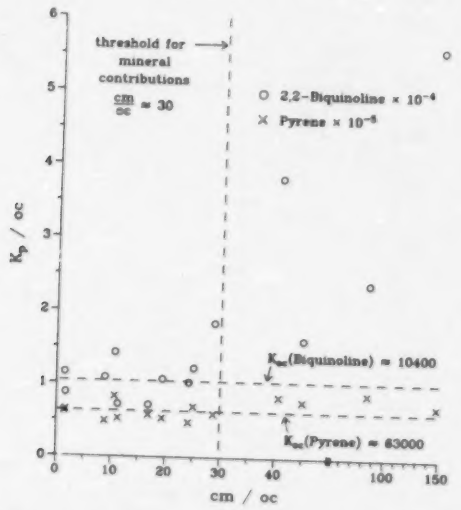

FIG. 2.—Mineral Contributions to Sorption—Biquinoline, Pyrene

enhancement even in highly mineral sediments. Means et al. (38) observed mineral-enhanced sorption (similar to biquinoline) for polynuclear aromatic hydrocarbons containing amino- and carboxy-substituents. An important feature of these data is the existence of a threshold for onset of mineral contributions. That is, for $cm/oc < 30$, mineral contributions are masked, regardless of the mineral content. This is consistent with the hypothesis of mineral blockage by organic matter, advanced by Hance (18), Walker and Crawford (59), and others (15).

Similar behavior would be expected for many pesticides sorbed to soils, but few studies have spanned a range in relative clay/organic content sufficient to examine this phenomenon. Partition coefficients for simazine [computed from the data of Harris and Sheets (20)] do reveal a similar trend, however (Fig. 3). For these data *cm* denotes total clay, *om* denotes organic matter fraction, and K_{om} is analogous to K_{oc}, indexed to organic matter. Again, for $cm/om < 15$ (which corresponds to $cm/oc < 30$), minerals do not appear to contribute to sorption.

Walker and Crawford (59) investigated triazine sorption on 32 soils and found the sorption of neutral compounds highly correlated with organic carbon (0.1%–27.1% range in carbon). Only one soil exceeded in mineral content the "threshold" described previously for simazine. For this soil, the organic carbon mediated sorption ($K_{oc} \times oc$) was approximately an order of magnitude less than observed partition coefficients. The studies of Wahid and Sethunathan show similar behavior for parathion (57) and BHC isomers (58).

This masking of mineral sorption by organic matter rationalizes the often found dichotomy where pollutants can sorb strongly to isolated minerals (i.e., sorption comparable to or exceeding that to natural soils/

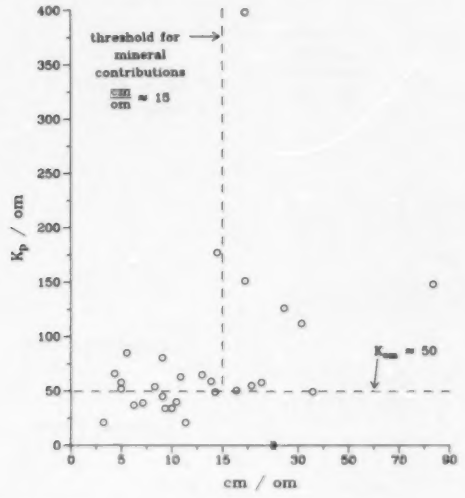

FIG. 3.—Mineral Contributions to Sorption—Simazine

sediments) yet show organic carbon controlled sorption to sediments—that is, linear dependence of sorption on organic carbon content (50).

In order to quantify mineral contributions, the functional dependence of f_a^{cm} on the relative amounts of mineral and organic carbon must be specified. If one assumes that the association of organic matter and minerals is a linear process of finite capacity, an appropriate model could define

$$f_a^{cm} = \frac{1}{1 + b\dfrac{oc}{cm}} \quad \ldots\ldots (29)$$

in which b describes the "effectiveness" of mineral blockage by organic matter at low surface coverage. The most direct quantification of this blocking phenomenon can be derived from changes in sorption effected by organic carbon removal. From Eq. 28, this change in partitioning (ΔK_p), is given by

$$\Delta K_p = K_{oc}\,\Delta oc + K_m cm\,\Delta f_a^m \quad \ldots\ldots (30)$$

in which it is *assumed* that partitioning to the remaining carbon (K_{oc}), and to the exposed mineral (K_m) are unaltered by the oc removal process. For complete removal of organic matter

$$\Delta K_p = K_{oc} \times oc + K_m cm\,(f_a^{cm} - 1) \quad \ldots\ldots (31)$$

in which oc and f_a^{cm} describe the parent sediment. What is frequently observed for these types of experiments is ($\Delta K_p << K_{oc} \times oc$), which can only occur if $f_a^{cm} < 1$ (Ref. 59), in which case the loss in sorption effected by oc removal is compensated by enhanced mineral sorption. For sorbates containing polar functional groups, an increase in sorption is often observed upon removal of organic carbon. Hassett, et al. (23), found for acetophenone sorption on the sediments/soils in Table 1 when cm/oc in the parent sediment exceeded 40, the removal of organic carbon resulted in an increase in sorption, and conversely, for $cm/oc < 40$, oc removal produced a decrease in sorption. If the blocking model (Eq. 29) is incorporated in Eq. 31, one can show when

$$\frac{oc}{cm} \gtrless \frac{K_m}{K_{oc}} - \frac{1}{b}, \quad \Delta K_p \gtrless 0 \quad \ldots\ldots (32)$$

For acetophenone, K_{oc}/K_m is approximately 20–25, which, combined with the observed inversion point for ΔK_p ($cm/oc \approx 40$), leads to an estimated b value of 50.

Assuming monolayer coverage of the mineral surface by organic matter, Walker and Crawford (59) estimated that 1% carbon would reduce the available mineral surface by 32 m^2/g, which corresponds to a 20%–30% decrease in surface area for typical swelling field-clays. This would estimate the blocking parameter (b) in the trial model to be 30–50, which is consistent with both the previous estimate derived from the acetophenone data and the observed thresholds for onset of mineral sorption described previously. It should be emphasized that such a blocking model

TABLE 1.—Sediments and Soils: Physical Properties

Number (1)	Location (2)	% O.C. (3)	pH (1:1) (4)	CEC me. 100 g (5)	Silt (6)	Clay (7)	Swelling clay (8)
4	Missouri River, Stanton, N. Dak.	2.07	7.79	23.7	41.8	55.2	40.1
5	Missouri River, Lake Oahe, N. Dak.	2.28	7.44	19.0	35.4	31.0	25.7
6	Missouri River, Big Bend Lake, S. Dak.	0.72	7.83	33.0	31.2	68.6	60.8
8	Missouri River, Onawa, Iowa	0.15	8.32	3.7	10.7	6.8	6.1
9	Loess sample, Turin, Iowa	0.11	8.34	12.4	75.6	17.4	16.3
13	Ohio River, Ceredo, W. Va.	3.04	6.90	11.86	27.1	52.6	—
14	Soil eroded hillside, Ceredo, W. Va.	0.48	4.54	18.9	34.4	63.6	13.8
15	Ohio River, Leavenworth, Ind.	0.95	7.79	11.3	48.7	35.7	10.1
18	Mississippi River, Columbus, Ky.	0.66	7.76	15.4	25.8	39.5	29.7
20	Soil, Fern Clyffe State Park, Ill.	1.30	5.50	8.5	71.4	28.6	21.9
21	Illinois River, Lorenzo, Ill.	1.88	7.60	8.3	42.7	7.1	2.8
22	Illinois River, Lacon, Ill.	1.67	7.55	8.5	52.7	21.2	14.8
23	Confluence of Illinois and Sangamon Rivers	2.38	6.70	31.2	13.6	69.1	57.6
26	Mississippi River, McClure, Ill.	1.48	7.75	20.9	55.4	42.9	37.1
B-2	Small stream, Watkinsville, Ga.	1.21	6.35	3.7	13.9	18.6	2.0

Note: Samples 4–26 collected and characterized by John Hassett and Wayne Banwart, B-2 collected by local EPA personnel and characterized by Hassett and Banwart.

should discriminate effective mineral surface, independent of the sorbate.

In this section a plausible method of factoring quantitatively pollutant sorption to mineral and organic components in sediments has been presented. The concept of mineral site blockage by natural organic matter and the associated model that enables quantification of the phenomenon, appear to reconcile a broad range of literature observations that might otherwise appear in conflict. These concepts remain tentative,

TABLE 2.—Mineral Contribution to Sorption

Compound type (1)	Neutral organics polar functional groups (2)	Nonpolar organics $< C_{10}$ (3)	Large nonpolar organics $> C_{10}$ (4)
K_m/K_{oc}	10–50	50–100	>100
"Threshold" for mineral contributions (cm/oc)	25–60	>60	insignificant in natural sediments

however, pending definitive testing.

Unfortunately, the sorption literature offers essentially no insight into estimation of mineral sorption contributions, K_m, in mixed, aged mineral suites typical of natural sediments. The reader is referred to a recent review of mineral versus organic contributions to sorption by Mingelgrin and Gerstl (41). In lieu of a quantitative estimator of mineral sorption, a semi-quantitative guide is offered for determining where and to what degree minerals may affect pollutant sorption (Table 2).

Nonhydrophobic Contribution to K_{oc}.—The presence of certain polar functional groups on a pollutant molecule can significantly alter its sorption properties relative to that prescribed by hydrophobic bonding. A most significant discrepancy is observed for aromatic amines, where neutral species sorption typically exceeds (5–10 fold) that estimated assuming hydrophobic bonding (23,25,38,42). Parris et al. (45) have proposed a reversible chemisorption of primary amines to natural organic matter (imine formation with humic carbonyl groups) that may account for this sorption enhancement. A converse effect (i.e., a reduction in sorption relative to hydrophobic bonding) has been observed for the negatively charged carboxylate group (23,38), which presumably derives from electrostatic repulsion in a negatively charged organic matrix.

The data of Means et al. (38) clearly demonstrate these phenomena. Fig. 4 shows their sorption data for 2-aminoanthracene and 6-aminochrysene on 12 of the sediments/soils in Table 1. [Sediments 8 and 9 were omitted because minerals dominated the sorption of these compounds on these sediments (38).] Measured partition coefficients are plotted versus partition coefficients estimated for hydrophobic bonding (i.e., K_p^h, computed via Eq. 21 using measured K_{ow}'s). The dashed line indicates concurrence with hydrophobic sorption. Both compounds showed excellent correlations of K_p with organic carbon content ($r^2 >$ 0.9 for these sediment/soils) with no apparent pH effects or ionic (anilinium) contributions. The pK_a's for these chemicals are 3.6 for aminoanthracene and 3.4 for aminochrysene which are one unit (in most cases two units) below sediment/soil pH's. Of note in these data are the consistent variations in measured sorption, relative to hydrophobic estimates.

As described in a previous section, if one chooses to factor sorption mechanisms within a given distribution volume of the sorbent, the proper combinatorial algebra would prescribe log-additivity of the factored contributions. That is

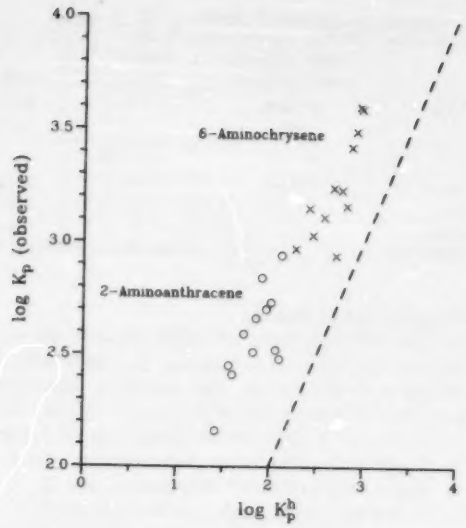

FIG. 4.—Nonhydrophobic Contributions to K_α

$$\log K_\alpha = \log K_\alpha^h + \sigma i \quad \ldots\ldots (33)$$

in which K_α^h and σi denote the hydrophobic and non-hydrophobic contribution, respectively.

The analogous equation for partition coefficients is

$$\log K_p = \log K_p^h + \sigma i \quad \ldots\ldots (34)$$

The data of Means et al. (Fig. 4) conform quite well to this equation with $\sigma NH_2 \approx 0.65$. The data suggest that the particular nonhydrophobic effects are not highly sediment dependent. In addition, the similarity in the sorption enhancement (NH_2) for both amino substituted compounds suggests that the effect may (as a first approximation) be indexed to the substituent, independent of the aromatic framework. Parris et al. (45) found the chemisorption of aromatic amines to be "blocked" by ring substitution (α to the amino group), but no sorption data are available to test this behavior for sediments or soils.

As was the case for mineral sorption contributions, this section prescribes a format for examining nonhydrophobic contributions to sorption on organic sediment components, but fails to give predictive insight into the magnitude of such effects. It is believed that the $-NH_2$ and $-SO_3^-$ groups represent positive and negative extremes for these phenomena, with deviations from hydrophobic estimates of K_p as large as an order of magnitude. Numerous other polar functional groups no doubt contribute, but it is doubtful that (excluding anionic constituents and nitrogenous base groups) the nonhydrophobic contribution will effect changes in sorption greater than a factor of two (i.e., $|\sigma_i| < 0.3$), relative to hydrophobic estimates.

Nonlinear Sorption Processes

Throughout this paper isotherm linearity has been generally assumed, which simplifies every aspect of sorption description, and facilitates the factoring of sorption behavior based on sorbent components and sorption mechanisms. If broad ranges in pollutant concentration are spanned, however, isotherms are in general nonlinear. In most instances, the assumption of linearity does not introduce large errors into descriptors of pollutant fate in the environment (48). The possible exceptions are: (1) The extrapolation of observed or estimated "linear" sorption behavior far out of the pollutant fugacity range of observation; and (2) strongly sorbed pollutants bound by highly site-specific mechanisms. It is worthwhile examining common nonlinear isotherm forms as well as the potential sources and ramifications of nonlinear sorption behavior.

From a thermodynamic viewpoint, conditions for non-linear behavior can be expressed in numerous ways. Previously it was stated that linearity required that pollutant fugacity must be a linear function of pollutant concentration in each phase (sorbed and solution) or that the fugacity coefficients (or activity coefficients) in each phase must be independent of pollutant concentration (Eq. 5). At pollutant concentrations common to aquatic systems (low ppm or less), one could expect aqueous phase activity coefficients to be constant unless pollutant levels approach solubility limits. In the sorbed phase, however, one could expect more substantive changes in activity coefficients if taken over broad ranges in pollutant loading. The functional dependence of the fugacity or activity coefficients on sorbed pollutant concentration could assume many forms depending on the "source" of the nonlinearity. For example, if the sorbed phase fugacity coefficient for the pollutant increases as some power of sorbed concentration (i.e., $\phi^s \propto S^m$, $m > 0$), the resulting isotherm form is Freundlich.

$$S \propto (\phi^w C)^{1/m+1} \quad \ldots\ldots (35)$$

in which the fugacity coefficient in the aqueous phase ϕ^w is assumed concentration invariant. In general, a monotonic increase in ϕ^s with increased concentration will result in an isotherm convex to the sorbed phase concentration axis. Conversely, similar behavior for ϕ^w (with constant ϕ^s) will result in a concave isotherm.

The representation of a composite isotherm in terms of component contributions (i.e., mineral, organic, etc.) is applicable to nonlinear sorption, but will generally produce very complex integrated isotherms. If one sorbent component dominates sorption, however, the resulting isotherm is that of the single component, multiplied by its active weight fraction. For example, if sorption is dominated by organic carbon and is described by a Freundlich isotherm, sorption to the whole sediment is given by

$$S = oc \times K_{oc}^f C^{1/n} \quad \ldots\ldots (36)$$

in which n = the conventional Freundlich parameter. K_{oc}^f, for a given pollutant, is frequently found to be sediment/soil independent (16,48), and is often equated with the analogous linear-case K_{oc}. For nonlinear (i.e., $n \neq 1$ or $m \neq 0$) versus linear isotherms, there are two key dis-

tinctions in these carbon referenced sorption parameters. First of all, as pointed out by Bowman (5) and others (23), the numerical value of K'_{oc} (or K_f, in which $K_f = K'_{oc} \times oc$) depends significantly upon the particular choice of concentration units for S and C. Standarization of units will facilitate comparing isotherms for different compounds and sorbents or both. Another important ramification of isotherm nonlinearity is that K'_{oc} is not a linear function of the aqueous phase activity coefficient (see Eq. 35), a fact that significantly complicates K'_{oc} extrapolation to other physical properties (i.e., K_{ow}, solubility, etc.) as was done for linear sorption. For a series of compounds with similar values of m, a plot of log K'_{oc} versus log K_{ow} should be linear with a slope approximating $1/(m + 1)$. This, in principle, can contribute to the wide range in "slope" parameters found in the literature for these types of relationships where highly polar compounds are involved (6,7).

Site-Specific Sorption.—If a pollutant (denoted C) "sorbs" at a specific type of site (denoted M), the process can be described by

$$C + M \overset{K}{\rightleftharpoons} S \quad \ldots\ldots (37)$$

in which S = the sorbed pollutant species. If the pollutant sorbs with a concomitant release of a competitive sorbate, the process can be further generalized to give

$$C + M \overset{K_{ex}}{\rightleftharpoons} S + C_j \quad \ldots\ldots (38)$$

in which C_j = the desorbed competitor. Although the aforementioned reactions assume 1:1 stoichiometry, any properly mass-balanced exchange coefficients may be incorporated.

The sorption exchange constant K_{ex} is given by

$$K_{ex} = \frac{SC_j}{MC} \quad \ldots\ldots (39)$$

in which all species descriptors refer to their respective equilibrium concentrations, with the same conventions as used previously (i.e., sorbent-associated concentrations expressed per unit sorbent mass; solution species expressed per unit aqueous phase volume).

M, which denotes available sites (unoccupied by the pollutant), can be expressed as

$$M = S_{max} - S \quad \ldots\ldots (40)$$

in which S_{max} is the total concentration of sites of type M. If this expression is substituted into Eq. 39, the sorbed pollutant concentration is given by

$$S = \frac{S_{max}}{1 + \frac{C_j}{K_{ex}C}} \quad \ldots\ldots (41)$$

This isotherm, which is in the form of the competitive Langmuir, is in general nonlinear (i.e., as S relates to C) and becomes linear in the limit

$$\frac{C_j}{K_{ex}C} >> 1 \quad \ldots\ldots (42)$$

which is the "low loading" limit corresponding to $S << S_{max}$. In this limit the linear partition coefficient, K_p, is given by

$$K_p = \frac{S_{max} K_{ex}}{C_f} \quad \text{(43)}$$

Because site-specific bonding to natural sorbents frequently involves weak-acid sites, S_{max} and C_f can vary in a complex fashion with system pH and sorbent concentration, a condition that vastly complicates estimation of site specific bonding contributions. Another complication for natural sediments derives from site-heterogenity both within and among the various sorbent components, with each type of site characterized by its own set of sorption parameters (S_{max}, K_{ex}, and C_f). In light of these complexities, current efforts in modeling metal binding to natural humics are developing conti uum models for humic sites describing the frequency distribution of sites and binding strengths (G. M. Perdue, Ga. Inst. of Tech., personal communication).

For uncharged "organics," the sorption contribution due to site-specific binding is lessened substantially by the competitive role of water in the sorption process. Given a definite sorptive preference for a polar pollutant over water (i.e., a large K_{ex}), the high concentration of water will significantly reduce site-specific binding. In aquatic systems, highly site specific pollutant sorption is likely to be of significance only where chemisorptive or ionic mechanisms are involved.

Sorption Kinetics.—A great deal of confusion exists in the sorption literature regarding the speed of attainment of sorption equilibrium. Sorption is often described as rapid and readily reversible (times to reach equilibrium of minutes to a few hours). Yet analytical chemists commonly encounter extreme difficulty extracting pollutants from field soils or sediments. For example, quantitative recovery of paraquat from a field soil requires, in effect, chemical "dissolution" of the sorbent matrix to achieve chemical release (28). Similarly, highly sorbed hydrophobic compounds frequently require lengthy extraction periods (days), multiple solvents, abrasive mixing techniques (or a combination thereof) for quantitative chemical recovery.

A concept long held by soil chemists [see Rao et al. (48,49) for a review of isotherm nonsingularity], and recently revamped for pollutant sorption to sediments (14), distinguishes the relative rates of the forward (adsorption) versus the reverse (desorption) process. DiToro and Horzempa (14) found for the sorption of a hexachlorobiphenyl to various sorbents (sediments, clays, silica) that the adsorption process was rapid (minutes to hours), but for the reverse process, a significant portion (~0.5) of the sorbed chemical was highly "resistant" to release. Conventional partition coefficients were factored into reversible and release-resistant components, based on hysteresis analysis.

Karickhoff (26) reported a somewhat similar finding for polynuclear aromatic hydrocarbons where the adsorption process *appeared* very rapid—that is, 35%–60% of the equilibrium sorption was achieved in minutes (mixing limited) with apparent equilibrium after a few hours. Also, a drastic change in the ease of extraction of sorbed chemical was frequently observed with increased incubation time. After short incubation periods (<5 minutes) essentially all (>90%) of the sorbed chemicals could

be easily extracted from the sediments by direct extraction of the suspensions with hexane for approximately 3 minutes. The fraction of sorbed chemical recovered by this brief extraction decreased to 0.5 after 3–5 hr of incubation and continued to decrease slowly over the next few days, leveling out in the range of 0.2–0.4.

All of these findings are suggestive of an intraparticle process whereby chemical is slowly incorporated into either particle aggregates or sorbent components. If one measures simply changes in aqueous phase and sorbed phase concentrations, the process appears to be complete after a few hours, but in reality may proceed indefinitely.

As found by DiToro and Horzempa (14) and others (48,49), the "nonlabile" character of the desorptive process is much more in evidence. For many compounds, desorption kinetics can be followed by continuously sparging the chemicals from sediment suspensions and measuring the temporal release profile. Fig. 5 shows the fraction of total hexachlorobenzene released as a function of time. The zero time intercept is measured aqueous phase chemical (prepurge). All the hydrophobic chemicals tested that were amenable to sparging could be recovered quantitatively (i.e., no irreversible binding), but the sparging time required was highly variable between compounds. Sorbed naphthalene was recovered (>90%) in minutes to a few hours; trifluralin required 20–50 hr; pentachloro and hexachlorobenzene required 10–30 days. For extended purges, it is uncertain what role sediment particle abrasion may play in effecting release, but release rates were not highly sensitive to gas flow rate (above the threshold gas flow required for desorption control of chemical flux from the suspensions). For many sediments, solids

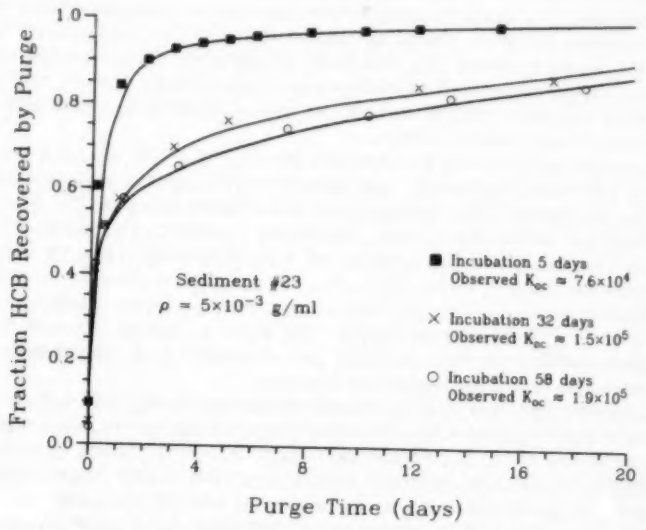

FIG. 5.—Release of Hexachlorobenzene from Sediments

concentration impacts significantly the rates of chemical uptake and release. The phenomenon appears to involve the formation of sediment aggregates even at low solids concentrations (i.e., 1 g/L) that severely retards the sorption process.

Insight into the nature of the "nonlabile" or resistant sorbed state can be gained from the relative ease of pollutant extraction by various nonaqueous solvents. Freeman and Cheung (17) suggested that the sorbed pollutant is physically incorporated into organic matter and that facility of solvent extraction is related to the ability of the solvent to swell the humin-kerogen polymer structure of the natural organic matter. Maximum swelling and therefore optimum release is achieved when the solubility parameter (denoted δm) of the extracting solvent approximates that characteristic of the sorbent.

Using trial solvents, ($6.9 > \delta_m > 14.5$), they found the most effective release of di(2-ethylhexyl)-phthalate from natural sediment in the case of dichloromethane ($\delta_m = 9.7$), which suggests the characteristic solubility parameter for natural organic matter in sediments to be approximately 10. This is not an entirely fortuitous result because the "physical mimicry" of octanol ($\delta_m = 10.3$) for natural organic matter is well established. As previously mentioned, however, DiToro and Horzempa (14) found "resistant" sorption to clays as well as sediments, so apparently other processes in addition to pollutant incorporation into organic matter are involved.

Quantitative modeling of sorption kinetics has been at best only marginally successful. In addition to the "quasi equilibrium" models of DiToro and Horzempa (14), Karickhoff (26) proposed a two stage kinetic model whereby sorption was factored into "labile" (occurring roughly within an hour) and nonlabile components (denotes S_1 and S_{n1}, respectively). The "labile" component was treated as equilibrium (K_1), and access to and from the "nonlabile" state was described by a mass transfer coefficient (k_d).

$$C \overset{K_1}{\rightleftharpoons} S_1 \overset{k_d}{\rightleftharpoons} S_{n1} \qquad (44)$$

For a given pollutant the fraction of the total sorption which was labile (i.e., K_1/K_p) varied from 0.2–0.6 for various sediments. The value of k_d was also quite variable among sediments, especially for highly sorbed chemicals (where a 3 fold variation was not uncommon). However, as a "rule of thumb" the characteristic time ($1/k_d$) for diffusive release from the "nonlabile" state approximates numerically the K_{oc} (in minutes).

A limitation of this model derives from the assumption of isotropic pollution distribution (with respect to pollutant fugacity) within each compartment (solution, "labile" sorbed, "nonlabile" sorbed). The model will not describe accurately sorption perturbations occurring in time periods which are short compared to the characteristic time for pollutant exchange with the "nonlabile" compartment (which may be hours to weeks for different compounds).

Current knowledge of this process (or processes) is incomplete or in some cases conflicting, but this author is very perplexed by the failure of most sorption reports to acknowledge any evidence of a "resistant" sorption component.

Dependence of Sorption on Temperature and Ionic Strength

It is convenient to factor the temperature dependence of sorption into sorbed and solution components because, for hydrophobic chemicals, the temperature dependence derives predominantly from the pollutant aqueous phase activity coefficient. This temperature dependence can thus be related to changes in pollutant solubility with temperature via Eq. 12. For linear sorption

$$\frac{K_p(T_2)}{K_p(T_1)} \approx \frac{X_s(T_1)}{X_s(T_2)} \exp - \frac{\Delta S_f}{R} T_m \left\{\left[\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]\right\} \quad \text{..... (45)}$$

in which T_2, T_1, T_m are in °K; $T \equiv T_m$ for liquids; $T < T_m$; $\Delta S_f/R \approx 6.5$ (described previously). Thus, given the melting point and appropriate pollutant solubilities, one can infer the change in sorption with temperature. Following this rationale, Kipling (32) suggested that if solution concentrations of pollutant were expressed, not in absolute value, but relative to pollutant solubility (i.e., C/X_s, defined as reduced concentrations, C_r), the resulting isotherms would be temperature independent.

For the linear case the reduced partition coefficient, K_p^r, is equal to $K_p \times X_s$. From Eq. 45

$$\frac{K_p^r(T_2)}{K_p^r(T_1)} \approx \exp - \left\{6.5\, T_m \left[\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]\right\} \quad \text{..... (46)}$$

or, reduced partition coefficients are temperature independent for liquids or for temperatures approaching the melting point. The ignorance of crystal energy contributions has created some confusion in interpreting the temperature dependence of sorption (via reduced isotherms) in the soils/pesticide literature (40).

Typically, the solubility of organic liquids (or solids, subcooled liquid referenced) increases slightly with increased temperature, and thus K_p is expected to decrease slightly with increased temperature (described by Eq. 45). For highly hydrophobic compounds, a significant increase in sorption with increased temperature is frequently observed (61). This may be the result of kinetically limited sorption, for which case increased temperature increases the rate of pollutant access to the "nonlabile" sorption compartment.

Sorption Dependence on Inorganic Electrolytes.—For site-specific competitive sorption, inorganic ions are often directly involved in the sorption process (Eq. 38). For most neutral pollutants, however, the predominant "salt" effect derives from the aqueous phase activity coefficient. As was the case with temperature dependence, this salt effect can be extrapolated directly from solubility via the Setschenow equation, which prescribes

$$\log \frac{X_s(I_2)}{X_2(I_1)} = -K_s(I_2 - I_1) \quad \text{..... (47)}$$

in which I_2, I_1 = salt concentrations and K_s = the Setschenow constant for a given salt (for example, $K_s \approx 0.16$ L/mole for NaCl). For salt mixtures, the solubility effect is frequently cumulative.

$$\Delta \log S_s = -\sum_i K_s^i (I_2^i - I_1^i) \quad (48)$$

For the linear sorption case, the dependence on salt content can be approximated by

$$\frac{K_p(I_2)}{K_p(I_1)} = \frac{X_s(I_1)}{X_s(I_2)} \quad (49)$$

$$\text{or} \quad \log \frac{K_p(I_2)}{K_p(I_1)} = K_s(I_2 - I_1) \quad (50)$$

in which the salt concentrations are aqueous phase values. Depending upon the sign of K_s, $\log K_p$ can vary directly or inversely with salt concentration. Because K_s is positive for most common salts, an increase in hydrophobic sorption with increased salt concentration is more typical. For example a 0.5 molar increase in NaCl concentration (~ seawater) would increase the sorption K_p by a factor of $10^{0.08}$ approximately 1.2. This is the converse effect to that seen in the competitive sorption case where increasing the concentration of a competitive electrolyte would decrease pollutant sorption.

Summary

The sorption properties of organic pollutants in aquatic systems are reviewed with emphasis on a priori estimation of sorption behavior utilizing commonly measured (or computed) physical properties of pollutants and sorbents, and incorporating commonly measured environmental variables.

For uncharged organic chemicals, binding to natural sorbents is dominated by "hydrophobic interactions." The key thermodynamic property discriminating the sorption of different chemicals is the aqueous phase activity coefficient, which is a measure of a chemical's affinity for water. That is, all hydrophobic chemicals have roughly the same affinity for a given natural sorbent surface, with affinity for water determining differences in sorption behavior. For composite sorbents, the organic matter constituent dominates sorption of uncharged chemicals. Partition coefficients, indexed to carbon content (i.e., K_{oc}), are relatively independent of other sediment/soil characteristics or geographic origin. Hydrophobic contributions to sorption can be a priori estimated from any pollutant property that relates directly to aqueous phase activity coefficient (such as solubility, octanol/water partition coefficient, solubility parameters, etc.).

Nonhydrophobic contributions to sorption, although generally of secondary importance, may be significant (or dominate) in some instances and tend to occur with one or both of the following conditions: (1) High sorbate polarity; and (2) low organic carbon content of the sorbent, especially with coincident high clay content. Although a priori estimation techniques comparable to hydrophobic sorption are not presently available, hydrophilic contributions relative to *Koc* can be estimated, based on chemical class and sorbent composition.

Pollutant sorption to sediment or soil is generally viewed as a rapid

process, although true sorption equilibrium may require weeks (to months) to achieve. Pollutant uptake and release kinetics are highly dependent on molecular size, sorbent cohesive properties, and solids concentration.

An area of particular current concern is the frequently observed dependence of "equilibrium" partitioning on solids concentration. For uncharged pollutants, the author attributes this phenomenological behavior to: (1) Sorption kinetics (i.e., failure to achieve sorption equilibrium which depends significantly on solids concentration); (2) colloid "interference" (i.e., failure to correct aqueous phase pollutant concentrations for colloid-bound chemical); and (3) measurement artifact (i.e. failure to account for alternate chemical sinks at low solids concentrations). Considerable research effort is currently being focused on this aspect of pollutant sorption behavior.

Appendix.—References

1. Bailey, G. W., and White, J. L., "Review of Adsorption and Desorption of Organic Pesticides by Soil Colloids, with Implications Concerning Pesticide Bioactivity," *Journal of Agricultural and Food Chemistry*, Vol. 12, 1964, pp. 324–332.
2. Bailey, G. W., and White, J. L., "Factors Influencing the Adsorption, Desorption, and Movement of Pesticides in Soil," *Residue Reviews*, Vol. 32, 1970, pp. 29–92.
3. Bark, L. S., and Graham, J. T., "Studies in the Relationship Between Molecular Structure and Chromatographic Behaviour, VIII. The Reversed Phase Thin-Layer Chromatography of some Halogenated Phenols and some Halogeno-; Alkyl-Substituted Phenols," *Journal of Chromatography*, Vol. 25, 1966, pp. 357.
4. Baughman, G. L., and Paris, D. F., "Microbial Bioconcentration of Organic Pollutants from Aquatic Systems—A Critical Review," *CRC Critical Reviews in Microbiology*, 1981, pp. 205–228.
5. Bowman, B. T., "Conversion of Freundlich Adsorption K Values to the Mole Fraction Format and the use of S_x Values to Express Relative Adsorption of Pesticides," submitted to *Soil Science Society of America Journal*, Vol. 46, 1982, pp. 740–743.
6. Briggs, G. G., "A Simple Relationship between Soils Adsorption of Organic Chemicals and Their Octanol/Water Partition Coefficients," *Proceedings*, 7th British Insecticide and Fungicide Conference, Nov., 1973, pp. 83–86.
7. Briggs, G. G., "Theoretical and Experimental Relationships between Soil Adsorption, Octanol-Water Partition Coefficients, Water Solubilities, Bioconcentration Factors, and the Parachor," *Journal of Agriculture and Food Chemistry*, Vol. 29, 1981, pp. 1050–1059.
8. Brown, D. S., and Combs, G., "A Model for Predicting Sorption of Organic Cations in Soils and Sediments," submitted to *Journal of Environmental Quality*, 1982.
9. Brown, D. S., and Flagg, E. W., "Empirical Prediction of Organic Pollutant Sorption in Natural Sediments," *Journal of Environmental Quality*, Vol. 10, No. 4, 1981, pp. 382–386.
10. Burchill, S., Greenland, D. J., and Hayes, M. H. B., "Adsorption of Organic Molecules," In *The Chemistry of Soil Processes* (Greenland and Hayes, eds.), Wiley, Chichester, England, 1981, pp. 221–400.
11. Carter, C. W., and Suffet, I. H., "Binding of DDT to Dissolved Humic Materials," *Environmental Science and Technology*, Vol. 16, No. 11, 1982, pp. 735–740.
12. Chiou, C. T., Peters, L. J., and Freed, V. H., "A Physical Concept of Soil-Water Equilibria for Nonionic Organic Compounds," *Science*, Vol. 206, No. 16, 1979, pp. 831–832.

13. Chou, S. J., Griffin, R. A., and Chou, M. M., "Effect of Soluble Salts and Caustic Soda on Solubility and Adsorption of Hexachlorocyclopentadiene," *Proceedings of the Eighth Annual Research Symposium*, U.S. Environmental Protection Agency, EPA-600/9-82-002, Cincinnati, Ohio, 1982, pp. 137–149.
14. DiToro, D. M., and Horzempa, L. M., "Reversible and Resistant Components of PCB Adsorption-Desorption: Isotherms," *Environmental Science and Technology*, Vol. 16, No. 9, 1982, pp. 594–602.
15. Edwards, A. P., and Bremner, J. M., "Microaggregates in Soils," *Journal of Soil Science*, Vol. 18, No. 1, 1967, pp. 64–73.
16. Farmer, W. J., "A Literature Survey of Benchmark Pesticides," Contract No. 68-01-2889, Criteria and Evaluation Div., OPP, U.S. Environmental Protection Agency, 1976.
17. Freeman, D. H., and Cheung, L. S., "A Gel Partition Model for Organic Desorption From a Pond Sediment," *Science*, Vol. 214, 1981, pp. 790–792.
18. Hance, R. J., "Influence of pH, Exchangeable Cation and the Presence of Organic Matter on the Adsorption of some Herbicides by Montmorillonite," *Canadian Journal of Soil Science*, Vol. 49, 1969, pp. 357–364.
19. Haque, R., "Role of Adsorption in Studying the Dynamics of Pesticides in a Soil Environment," *Environmental Dynamics of Pesticides* (edited by R. Haque and V. Freed), Plenum Press, New York, N.Y., 1975, pp. 97–113.
20. Harris, C. I., and Sheets, T. J., "Influence of Soil Properties on Adsorption and Phytotoxicity of CIPC, Diuron, and Simazine," *Weeds*, Vol. 13, 1965, pp. 215–219.
21. Harris, C. I., and Warren, G. F., "Adsorption and Desorption of Herbicides by Soil," *Weeds*, Vol. 12, 1964, pp. 120–126.
22. Hassett, J. J., Means, J. C., Banwart, W. L., Wood, S. G., Ali, S., and Khan, A., "Sorption of Dibenzothiophene by Soils and Sediments," *Journal of Environmental Quality*, Vol. 9, No. 2, 1980, pp. 184–186.
23. Hassett, J. J., Means, J. C., Barnwart, W. L., and Wood, S. G., "Sorption Properties of Sediments and Energy-Related Pollutants," U.S. Environmental Protection Agency, No. EPA-600/3-80-041, 1980.
24. Hassett, J. P., and Anderson, A. A., "Effects of Dissolved Organic Matter on Adsorption of Hydrophobic Organic Compounds by River and Sewage Borne Particles, *Water Research*, Vol. 16, 1982, pp. 681–686.
25. Hsu, T., and Bartha, R., "Interaction of Pesticide-Derived Chloroaniline Residues with Soil Organic Matter," *Soil Science*, Vol. 116, No. 6, 1974, pp. 444–452.
26. Karickhoff, S. W., "Sorption Kinetics of Hydrophobic Pollutants in Natural Sediments," Contaminants and Sediments, Vol. 2 (ed. R. A. Baker), Ann Arbor Science Publishers, Inc., Ann Arbor, Mich., 1980, pp. 193–205.
27. Karickhoff, S. W., "Semi-Empirical Estimation of Sorption of Hydrophobic Pollutants on Natural Sediments and Soils," *Chemosphere*, Vol. 10, 1981, pp. 833–846.
28. Karickhoff, S. W., and Brown, D. S., "Paraquat Sorption as a Function of Particle Size in Natural Sediments," *Journal of Environmental Quality*, Vol. 7, No. 2, 1978, pp. 246–252.
29. Karickhoff, S. W., Brown, D. S., and Scott, T. A., "Sorption of Hydrophobic Pollutants on Natural Sediments," *Water Research*, Vol. 13, 1979, pp. 241–248.
30. Kenaga, E. E., and Goring, C. A. I., "Relationship between Water Solubility, Soil Sorption, Octanol-Water Partitioning and Bioconcentration of Chemicals in Biota," *3rd Aquatic Toxicology Symposium, Proceedings of the American Society for Testing and Materials*, No. STP 707, 1978, pp. 78–115.
31. Khan, S. U. "Adsorption of Pesticides by Humic Substances. A Review," *Environmental Letters*, Vol. 3, No. 1, 1972, pp. 1–12.
32. Kipling, J. J., "Adsorption from Solutions of Non-Electrolytes," Academic Press, Inc., London, England, 1965, 310 pp.
33. Lambert, S. M., "Functional Relationship between Sorption in Soil and

Chemical Structure," *Journal of Agricultural and Food Chemistry*, Vol. 15, No. 4, 1967, pp. 572–576.
34. Leo, A. J., "Calculation of Partition Coefficients Useful in the Evaluation of the Relative Hazards of Various Chemicals in the Environment," in I. J. C. Symposium on Structure Activity Correlations in Studies of Toxicity and Bioconcentration with Aquatic Organisms (Veith, G. D., ed.), International Joint Commission, Konasewich, D., Secretariat, Windsor, Ontario, 1975.
35. Leo, A., Hansch, C., and Elkins, D., "Partition Coefficients and Their Uses," *Chemical Reviews*, Vol. 71, No. 6, 1971, pp. 525–616.
36. Macalady, D. L., and Wolfe, N. L., "Effects of Sediment Sorption on Abiotic Hydrolyses: I. Organophosphorothioate Esters," submitted to *Environmental Science and Technology*, 1982.
37. Mackay, D., "Finding Fugacity Feasible," *Environmental Science and Technology*, Vol. 13, 1979, pp. 1218–1223.
38. Means, J. C., Wood, S. G., Hassett, J. J., and Banwart, W. L., "Sorption of Amino- and Carboxy-Substituted Polynuclear Aromatic Hydrocarbons by Sediments and Soils," *Environmental Science and Technology*, Vol. 16, No. 2, 1982, pp. 93–98.
39. Means, J. C., Wood, S. G., Hassett, J. J., and Banwart, W. L., "Sorption of Polynuclear Aromatic Hydrocarbons by Sediments and Soils," *Environmental Science and Technology*, Vol. 14, 1980, pp. 1524–1531.
40. Mills, A. C., and Biggar, J. W., "Solubility-Temperature Effects on the Adsorption of Gamma- and Beta-BHC from Aqueous and Hexane Solutions by Soil Materials," *Soil Science Society of America Proceedings*, Vol. 33, 1969, pp. 210–216.
41. Mingelgrin, U., and Gerstl, Z., "Reevaluation of Partitioning as a Mechanism of Nonionic Chemicals Adsorption in Soils," *Journal of Environmental Quality*, Vol. 12, No. 1, 1983, pp. 1–11.
42. Moreale, A., and VanBladel, R., "Influence of Soil Properties on Adsorption of Pesticide-Derived Aniline and p-chloraniline, *Journal of Soil Science*, Vol. 27, 1976, pp. 48–57.
43. Nkedi-Kizza, P., Rao, R. S. C., and Johnson, J. W., "Adsorption of Diuron and 2,4,5-T on Soil Particle-Size Separates," submitted to the *Journal of Environmental Quality*, 1982, Vol. 12, No. 2, 1983, pp. 195–197.
44. O'Conner, D. J., and Connolly, J. P., "The Effect of Concentration of Adsorbing Solids on the Partition Coefficients," *Water Research*, Vol. 14, 1980, pp. 1517–1523.
45. Parris, G. E., "Covalent Binding of Aromatic Amines to Humates. 1. Reactions with Carbonyls and Quinones," *Environmental Science and Technology*, Vol. 14, No. 9, 1980, pp. 1099–1106.
46. Pierce, J., and Wolfe, N. L., "Effects of Sediment Sorption on Abiotic Hydrolyses: II 4-(p-Chlorophenoxy)butylbromide," submitted to *Environmental Science and Technology*, 1983.
47. Prausnitz, J. M., "Molecular Thermodynamics of Fluid-Phase Equilibria," Prentice-Hall International Series in the Physical and Chemical Engineering Sciences, Englewood Cliffs, N.J., 1969, 523 pp.
48. Rao, P. S. C., Davidson, J. M., Berkheiser, V. E., Ou, L. T., Street, J. J., Wheeler, W. B., and Yuan, T. L., "Retention and Transformation of Selected Pesticides and Phosphorous in Soil-Water Systems: A Critical Review," USEPA, EPA-600/3-82-060, Athens, Ga., 1982.
49. Rao, P. S. C., Davidson, J. M., and Kilerease, D. P., "Examination of Nonsingularity of Pesticides Adsorption-Desorption Isotherms for Soil Pesticide Systems," Agronomy Abstracts, Vol. 34, 1982.
50. Rogers, R. D., McFarlane, J. C., and Cross, A. J., "Adsorption and Desorption of Benzene in Two Soils and Montmorillonite Clay," *Environmental Science and Technology*, Vol. 14, No. 4, 1980, pp. 457–460.
51. Schwarzenbach, R. P., and Giger, W., "Behaviour and Fate of Halogenated Hydrocarbons in Ground Water."
52. Schwarzenbach, R. P., and Westall, J., "Transport of Non-Polar Organic

Compounds from Surface Water to Groundwater," *Environmental Science and Technology*, Vol. 15, No. 11, 1981, pp. 1360–1367.
53. Steen, W. C., and Karickhoff, S. W. "Biosorption of Hydrophobic Organic Pollutants by Mixed Microbial Populations," *Chemosphere*, Vol. 10, 1981, pp. 27–32.
54. Sullivan, J. D., and Felbeck, G. T., "A Study of the Interaction of *S*-Triazine Herbicides with Humic Acids from Three Different Soils," *Soil Science*, Vol. 106, No. 1, 1968, pp. 42–51.
55. Talbert, R. E., and Fletchall, O. H., "The Adsorption of some *S*-Triazines in Soils," *Weeds*, Vol. 13, 1965, pp. 46–52.
56. Voice, T. C., and Weber, W. J., "Sorption of Hydrophobic Compounds by Sediments and Suspended Solids in Aquatic Systems I: Theory and Background," *Water Research*, 1982.
57. Wahid, P. A., and Sethunathan, N., "Sorption-Desorption of Parathion in Soils," *Journal of Agricultural and Food Chemistry*, Vol. 26, No. 1, 1978, pp. 101–105.
58. Wahid, P. A., and Sethunathan, N., "Sorption-Desorption of α, β, and γ Isomers of Hexachlorocyclohexane in Soils," *Journal of Agricultural and Food Chemistry*, Vol. 27, No. 5, 1979, pp. 1050–1053.
59. Walker, A., and Crawford, D. V., "The Role of Organic Matter in Adsorption of the Triazine Herbicides by Soils," *Proceedings from the Symposium of Radiation in Soil Organic Matter Studies*, 1968, pp. 91–108.
60. Weber, J. B., "Mechanisms of Adsorption of *S*-Triazines by Clay Colloids and Factors Affecting Plant Availability," *Residue Reviews*, Vol. 32, 1970, pp. 93–130.
61. Weber, W. J., Voice, T. C., Pirbazari, M., Hunt, G. E., and Ulanoff, D. M., "Sorption of Hydrophobic Compounds by Sediments and Suspended Solids in Aquatic Systems II: Methods and Pilot Compound Results, *Water Research*, 1982.
62. Yalkowski, S. H., "Solubility and Partitioning V: Dependence of Solubility on Melting Point," *Journal of Pharmaceutical Science*, Vol. 70, No. 8, 1981, pp. 971–973.
63. Yalkowski, S. H., and Valvani, S. C., "Solubility and Partitioning I: Solubility of Non-electrolytes in Water," *Journal of Pharmaceutical Science*, Vol. 69, No. 8, 1980, pp. 912–922.
64. Zepp, R. G., and Schlotzhauer, P. F., "Effects of Equilibration Time on Photoreactivity of the Pollutant DDE Sorbed on Natural Sediments," *Chemosphere*, Vol. 10, No. 5, 1981, pp. 453–460.